

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Yury Gogotsi	**Confirmation No.: 1617**
Application No.: 10/561,768	**Group Art Unit: 1793**
Filing Date: March 23, 2006	**Examiner: Stuart L. Hendrickson**

For: NANOPOROUS CARBIDE DERIVED CARBON WITH TUNABLE PORE SIZE

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION PURSUANT TO 37 CFR § 1.132

I, Dr. Yury Gogotsi, declare as follows:

1) I am currently Director of the A.J. Drexel Nanotechnology Institute, Trustee Chair Professor of Materials Science and Engineeiring, Professor of Mechanical Engineering and Mechanics, and Professor of Chemistry at Drexel University. Previously, I have held positions as Associate Dean of the College of Engineering and Professor of Materials Science and Engineering at Drexel University and Associate Professor of Mechanical Engineering (with tenure) and Assistant Director, Research Resources Center at the University of Illinois at Chicago, Department of Mechanical and Industrial Engineering.

2) I have a D.Sc. in Materials Engineering from the National Academy of Sciences, Ukraine, a Ph.D. in Physical Chemistry from the Kiev Polytechnic Institute, Ukraine, and a Master's degree in Metallurgy, also from the Kiev Polytechnic Institute.

3) I am a Fellow in the American Association for Advancement of Science (AAAS), the Electrochemical Society, and the American Ceramic Society and have received numerous awards and accolades for my work in materials science including science of ceramics, carbon, nanomaterials, and nanofluidics. A full listing of my awards and recognitions is provided in my attached curriculum vitae.

4) I have co-authored or edited 14 books, authored or co-authored more than 200 peer-reviewed journal papers and 90 papers in proceedings, filed 35 patent applications, and presented more than 100 invited lectures and seminars.

5) My current research interested include the chemistry of nanomaterials, including carbon nanomaterials, nanofluidics, and devices made therefrom.

6) I have studied and am familiar with U.S. Patent Application Serial No. 10/561,768 (the above-identified application, hereinafter "the '768 Application"), on which I am listed as an inventor, and the prosecution history associated with it. I believe myself to be well qualified to provide comment on the subject matter under consideration.

7) I understand the claims of the '768 Application to be directed to a method of preparing nanoporous carbon whose nanopore diameters can be adjusted in increments as low as 0.05 to 0.2 nm, simply by variations in processing temperature.

8) I have been asked to comment on the state of the art at the time of the invention described in the '768 Application and on the ability to control the process parameters of the present invention. I will discuss each in turn.

9) In reviewing past office actions, it appears that the Examiner considered or considers the invention simply to be the ability to halogenate carbides so as to produce nanoporous carbon. Rather, I have discovered that, through careful selection and *control of processing temperatures, for a given carbide* precursor, it is possible to control and define the nanopore sizes and nanopore size distributions of the resulting carbon articles.

10) Until the discovery which forms the basis of this invention, the consensus of those skilled in the art was that subjecting a given carbide composition to halogenation at different elevated temperatures would provide a limited series of nanoporous compositions whose nanopore sizes varied by discrete "jumps" (or quanta), the distances of those "jumps" associated with the distance between graphitic layers; i.e., ca. 0.3-0.4 nm, such that the available pore sizes for a given carbide composition was limited to a finite number of pore sizes by the nature of the original carbide composition.

11) As but one example, Fedorov (Mendeleev Chemistry Journal, 39 (6) pp. 87-87) describes the "chlorination of metal carbides at high temperatures is among the number of quite well-studied and assimilated processes in non-ferrous metallurgy and the chemical industry," (page 88, line 3-4). Reporting on the range of work conducted at the Leningrad Institute of Technology during the period 1977-1992, which focused on the "[c]onditions of carbide chlorination . . . including a thermodynamic analysis of reactions and the experimental study of their kinetics as a function of such factors as temperature, reaction ratio, dispersion of carbides, and conditions of contact of carbide with chlorine," Fedorov describes *only* the impact of reaction ratio, dispersion of carbides, and conditions of contact of carbides with chlorine.

12) Similarly, Gordeev, *et al.* (WO 98/54111, page 7, line 26 through page 8, line 20) describes *inter alia* the prevailing thinking until the present invention:

> *Current notions of carbon material structure point out that nanopores generated during the thermochemical treatment process are* ***formed by ordered or disordered graphite planes of carbon****, which for simplicity might be considered as shaped slots,* ***the width of the latter depending on the type of carbide*** *used for forming of the workpiece with transport porosity.*

The same reference goes on to describe a formula for determining **nanopore sizes which depend exclusively on the nature of the carbide precursor.**

13) My discovery that it is possible to provide compositions from a given carbide precursor with much smaller differences, so as to "de-limit" the number of mean pore sizes available from a given carbide composition provides for the present invention of making nanoporous compositions whose mean nanopore diameters can be adjusted in increments of 0.05 to 0.2 nm, and with a precision of within 0.05 nm to a targeted value. In this way, it is possible to "tune" the final compositions, and such is implicit in the use of this term "tuneable." I am unaware or unable to find any evidence that such nanopore "de-limited tuning" has been previously described by varying halogenation temperature, either explicitly cited or necessarily inherent in, or taught by any of the art cited by the Examiner.

14) Because of this misunderstanding of the nature of potential "tunability" of nanopore size, no one in the industry, at least to my knowledge, even attempted to "tune" nanopore size to the specific degree as we are claiming by temperature alone, because no one thought it was possible

to do so or that such an attempt would succeed. I understand that, in the pending office action, the Examiner is citing Leis J., *et al.*, "Carbon nanostructures produced by chlorinating aluminum carbide," *Carbon*, 2001, 39, 2043-2048, alone and in combination with El-Raghy, *et al.*, *J. Appl. Phys.*, 1998, 83(1): 112-119, Boehm, *et al.*, Proc. 12^{th} Biennial Conf. on Carbon, 1975, pp. 149-150, and U.S. Patent 3,066,099, issued to Mohun, as rendering the present invention obvious. However, in my view, none of these references render the current claims obvious because it was not yet known possible to achieve the current invention at the time these references published.

14) Opposite the presently pending office action, I understand that the Examiner is taking the position that because the cited references show large variations in pore sizes associated with large changes in processing temperatures, and do not preclude the use of smaller temperature variations to achieve the levels of changes claimed in my current invention, that it would naturally follow that these same references teach or at least suggest the use of small temperature changes to achieve the instant results. But for the reasons given above, while such an approach may appear obvious ***retrospectively***, at the time of the instant invention, no one considered doing so, for the reasons stated above.

14) This "mental block" existed despite a long-felt need for a simpler method of manufacturing nanoporous carbon to specific pore nano-dimensions at the sub-nanometer scale. Several of the previously references described above and cited in previous office actions do show attempts to vary the resulting nanopore sizes by using ***compositional variations*** of the carbide precursors or by treating porous carbons bodies ***post-halogenation*** to achieve the same effects as described in this instant invention. But these are more complicated than the simple application of controlled temperature such as disclosed in the '768 Application.

15) As further evidence of the novelty of this invention, I note that that this invention has recently been recognized by R&D Magazine with the prestigious R&D 100 award, as one of the revolutionary technologies of 2009. This fact was pointed out to the Examiner in a previous office action.

16) Additionally, a search of Google Scholar reveals that this '768 Application has been cited in other published works more than 100 times, another indication as to the novelty of the invention.

17) Opposite the presently pending office action, I understand that the Examiner is characterizing the ability to reproducibly control nanopore diameter in range of "from about 0.05 nm to about 0.2 nm" as reading upon "an attempt to duplicate an experiment but having a small unavoidable minor temperature fluctuation between runs." However, I can personally attest that it is possible to control and deliberately vary nanopore size to within this tight window on a semi-commercial scale, and that such variances would be outside the bounds of "unavoidable minor temperature fluctuation between runs." In my laboratory, depending on the carbide precursor, such changes are associated with about 50-100°C changes at temperatures 200-1000°C. Such temperature variances are not "minor temperature fluctuations between runs." Commercial furnaces are capable of controlling temperatures well within these limits (usually, within 1-5 °C) and nowhere within the work zone of the furnace temperature fluctuations exceed 10 °C. Stated another way, variations in temperatures of less than 1-5°C, the levels to which commercial furnaces can be controlled, do not provide the variance in mean nanopore diameters described in the present claims.

18) I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information or belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful statements may jeopardize the validity of the application, any patent issuing thereupon, or any patent to which this verified statement is directed.

Date: August 30, 2010

Yury Gogotsi

Dr. Yury Gogotsi

Attachment

Partial Curriculum Vitae for Yury Gogotsi

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Education

D.Sc.	Materials Engineering, National Academy of Sciences, Ukraine, 1995
Ph.D.	Physical Chemistry, Kiev Polytechnic Institute, Ukraine, 1986
M.S.	Metallurgy, Kiev Polytechnic Institute, Ukraine, 1984

Professional Appointments

Drexel University, Department of Materials Science and Engineering

09/2008 – present	Trustee Chair Professor of Materials Science and Engineering
02/2003 – present	Director, A.J. Drexel Nanotechnology Institute
09/2002 – present	Assistant Professor, Professor of Chemistry
12/2002 – 9/2007	Associate Dean of the College of Engineering
11/2001 – present	Professor of Mechanical Engineering and Mechanics
08/2000 –08/2008	Professor of Materials Science and Engineering, University of Illinois at Chicago (UIC), Department of Mechanical Engineering
9/2001 – 8/2003	Adjunct Professor of Mechanical Engineering
6/1999 – 9/2000	Associate Professor of Mechanical Engineering (with tenure)
9/1999 – 8/2000	Assistant Director, UIC Research Resources Center
10/1996 – 5/1999	Assistant Professor of Mechanical Engineering

Current Research Interests

Chemistry of carbon nanomaterials, nanofluidics, electrochemical capacitors, Raman spectroscopy

Publications

2 books co-authored, 12 books edited, 15 book chapters, more than 200 journal papers, 90 papers in proceedings, 35 patents filed, more than 100 invited lectures and seminars.

Five Recent Related Publications:

1. J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, Monolithic Carbide-Derived Carbon Films for a New Generation of Micro-Supercapacitors, ***Science***, *238,* 480-48 (2010)
2. J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, Desolvation of ions in subnanometer pores, its effect on capacitance and double-layer theory, ***Angewandte Chemie Int. Ed.,*** *47* (18), 3392-3395 (2008)
3. C. Largeot, C. Portet, J. Chmiola, P.L. Taberna, Y. Gogotsi, P. Simon, Relation between the Ion Size and Pore Size for an Electric Double-Layer Capacitor, ***J. Am. Chem. Soc.*** *130* (9), 2730-2731 (2008)
4. P. Simon, Y. Gogotsi, Materials for Electrochemical Capacitors, ***Nature Materials***, *7*, 845-54 (2008)
5. J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, and P. L. Taberna, Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer, ***Science***, *313*, 1760-1763 (2006)

Other Important Related Publications:

6. T. Kyotani, J. Chmiola, Y. Gogotsi, Carbide Derived Carbon and Templated Carbons, Chapter 3 in ***Carbon Materials for Electrochemical Energy Storage Systems***, edited by F. Beguin and E. Frackowiak, CRC Press/Taylor and Francis, pp. 77-113 (2009).
7. J. Chmiola, Y. Gogotsi, Supercapacitors as Advanced Energy Storage Devices, ***Nanotechnology Law and Business***, *4*(1), 577-584 (2007)

8. Y. Gogotsi, A. Nikitin, H. Ye, W. Zhou, J.E. Fischer, B. Yi, H. C. Foley, M. W. Barsoum, Nanoporous carbide-derived carbon with tuneable pore size, ***Nature Materials***, *2* (9) 591–594 (2003)
9. Y. Gogotsi, S. Welz, D.A. Ersoy, M.J. McNallan, Conversion of Silicon Carbide to Crystalline Diamond-Structured Carbon at Ambient Pressure, ***Nature***, *411*, 283-287 (2001)
10. Y. Gogotsi, J. Libera, N. Kalashnikov, M. Yoshimura, Graphite Polyhedral Crystals, ***Science***, *290*, 317-320 (2000)

Professional Awards and Recognitions

2009 Fellow, American Association for Advancement of Science (AAAS)
2008 Fellow, The Electrochemical Society
2006 Innovator Award, NANO 50™, NASA Tech Briefs
2005 Fellow, American Ceramic Society
2005 Drexel University College of Engineering Outstanding Research Award
2004 Academician, World Academy of Ceramics
2003 R&D 100 Award from R&D Magazine (awarded again in 2009)
2003 R.B. Snow Award from the American Ceramic Society (re-awarded in 2005 and 2007)
2002 S. Somiya Award from the International Union of Materials Research Societies
2002 G.C. Kuczynski Prize from the International Institute for the Science of Sintering
2002 Elected Full Member, International Institute for the Science of Sintering
2002 Drexel University Research Achievement Award (awarded again in 2009)
2001 Winner of the Collegiate Inventors Competition, the National Inventors Hall of Fame
1999 University of Illinois-Chicago College of Engineering Faculty Research Award
1993 I.N. Frantsevich Prize from the Ukrainian Academy of Sciences
1993 – 1995 NATO/Norwegian Research Council Fellowship, University of Oslo, Norway
1992 – 1993 Japan Society for the Promotion of Science (JSPS) Fellowship, Tokyo Inst. Techn., Japan
1990 – 1992 Alexander von Humboldt Fellowship, University of Karlsruhe, Germany

Selected Synergistic Activities

Directed: 2 NSF IGERT, 2 NSF RET as PI and 2 NSF RET programs as Co-PI

Panel Co-Chair: *DOE Workshop on Basic Research Needs for Electrical Energy Storage*, 2007

Director:

NATO Advanced Research Workshop on Nanostructured Materials and Coatings for Biomedical and Sensor Applications, Kiev, Ukraine (2002); *NATO Advanced Study Institute on Materials Science of Carbides, Nitrides and Borides,* St. Petersburg, Russia (1998)

Coordinator: Mentorship Program with Illinois Academy of Math and Sciences, 1999/2000

Co-Director: *International Workshop on Hysteresis, Metastability and Aftereffect*, Chicago, IL (2000)

Guest Professor: University of Limoges, France (May-June 1994, June 1999, July 2005); Paul Sabatier University, Toulouse, France (Oct.-Dec. 2007)

Editorship:

Nanomaterials Handbook (CRC Press, Boca Raton) 2006, 800 pp.; *Carbon Nanomaterials* (CRC Press, Boca Raton) 2006, 326 pp; *CARBON* (Elsevier)

Associate Editor or a Member of the Editorial Board:

AZojomo - Journal of Materials Online, since 2005; Advances in Applied Ceramics, since 2005; British Ceramic Transactions, 2004, *International Journal of Applied Ceramic Technology*, 2003-2007; *Reviews in Advanced Materials Science*, since 2000; *Materials Physics and Mechanics*, since 2000; *Advances in Technology of Materials and Materials Processing Journal (ATM)*, since 1998; *J. Materials Processing and Manufacturing Science* (1997-2002); *Advanced Ceramics and Glass* (1992-1993)

Acted as reviewer:

Science, Nature, Nature Materials, Nature Nanotechnology, Nano Letters, Advanced Materials and other journals; The Petroleum Research Fund, Humboldt Foundation,

CNRS (France), DFG (Germany); National Research Council (NRC), Department of State, DOE, NSF and other agencies